Exploring Electrochemistry

PURPOSE

- Create a galvanic (Danielle) cell and determine the voltage generated by it
- Use the Nernst equation to calculate the concentration of an unknown solution in a galvanic cell
- Create a concentration cell and use the Nernst equation to calculate the concentration of an unknown solution
- Predict an activity series

INTRODUCTION

The branch of chemistry dealing with the exchange of electrons between two species is **electrochemistry**. The electrons move from the species oxidized to the species reduced. There are a number of mnemonic devices to help you to remember the direction of this flow of electrons. One of these is "***LEO*** the Lion says ***GER***," meaning

*L*oss of *E*lectrons is *O*xidation
and
*G*ain of *E*lectrons is *R*eduction

In a galvanic (or voltaic) cell, as you may recall from Experiment 16, chemical differences cause an electric change. Potential differences between substances cause electrons to flow from one species to another, as long as the half-cells are separated by a salt bridge and an external circuit. If the half-cells are in physical contact with each other, the potential difference is wasted as heat rather than as flow of electrons through an external circuit. In contrast to a galvanic cell, an electrolytic cell represents the opposite situation: an externally supplied electric current that forces chemical differences to occur.

The **electromotive force** ("emf") of a galvanic cell may be calculated by combining the values for each half-cell from a table of Standard Reduction Potentials ("SRP") to find E°, the **standard voltage** for the cell. The superscript ("°") indicates standard conditions of one atmosphere, 298 Kelvins, and one molar concentration of all species in solution. If any of these characteristics differs from the standard condition, then the voltage in the cell will be changed. To calculate the altered or nonstandard voltage, you can use the Nernst equation, developed by the Nobel laureate Walther Nernst. In the full form of the Nernst equation, a difference in any of these characteristics can be accommodated:

$$\mathrm{E} = \mathrm{E}^{\circ} - \left(\frac{RT}{nF}\right) \ln \mathrm{Q}$$

where E = nonstandard voltage; $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$; T = temperature in Kelvins; n = number of moles of electrons transferred in the redox; F = Faraday's constant (96,500 coulombs mol^{-1}); and Q = trial equilibrium reaction quotient, expressed as $\frac{[products]}{[reactants]}$.

But note: because ions in solution are not affected by pressure over the surface of the solution, and one frequently assumes the standard temperature of 298 K, there is a variant of the Nernst equation used to allow calculation with only a difference in concentrations of ions of the two half-cells. Keep in mind, also, that this form of the Nernst equation uses base-10 log rather than the natural log:

$$E = E^{o} - \left(\frac{0.0591}{n}\right)\log Q$$

Because the cell potential depends on the concentration of the ions in the two half-cells, you can construct a galvanic cell with identical half-cells except for the concentrations of the ions. This is called a **concentration cell.** The difference in voltage is apt to be small because all components of the half-cells are identical except for the concentrations. For example, the voltage between a 1.0 M Cu^{2+} solution half-cell and one of 0.010 M Cu^{2+} solution is just less than 0.06 V.

Experimentation with various metals and solutions containing the cations of those metals is fascinating. You can observe the behavior of such situations to establish an **activity series** of the ease of oxidation of certain metals. For example, if you place a piece of solid copper wire into a solution of silver nitrate, you will observe solid silver metal forming onto the copper wire (thus the reduction of Ag^+ to Ag), while the solution in the container becomes blue (thus Cu becomes Cu^{2+}). From this, you can conclude that copper is more easily oxidized than silver. You might verify this conclusion by dropping a piece of silver wire into a solution of Cu^{2+} and noticing that nothing happens, because the more easily oxidized copper is already oxidized.

Procedure Preview In this experiment, you will use the techniques of microchemistry to set up three different electrochemical cells and thus compare the behavior of three different half-cells paired with each other.

Pre-Lab Questions

1. What is a Danielle cell?
2. In a functioning galvanic cell
   a. at which electrode does oxidation occur? where does reduction occur?
   b. which electrode gains mass? which electrode loses mass?
   c. around which electrode does the concentration of cation solution increase?
   around which electrode does the concentration of cation solution decrease?
   d. from which electrode and to which electrode do electrons in the external circuit move?
3. What is the function of a salt bridge?
4. Has all chemistry ceased when the voltage of a galvanic cell becomes zero? Explain.

MATERIALS

- 24-well microplate
- 1 *M* $CuSO_4$
- 1 *M* $ZnSO_4$
- unknown *M* $CuSO_4$ solution
- 1 *M* KCl solution
- sandpaper (or steel wool)
- Cu metal strip
- Zn metal strip
- filter paper
- forceps
- voltmeter

PROCEDURE

I. Initial preparations

Step A Cut a piece of filter paper into a number of strips approximately 0.5 by 4.0 cm.

Step B Place the strips of filter paper into a small beaker containing 1 *M* KCl solution, allowing them to soak up the solution.

Step C Locate two strips of copper metal and one strip of zinc metal, each approximately 0.5 by 4.0 cm.

Step D Use fine sandpaper or steel wool to polish the metal strips. Try to clean off any external corrosion to leave a shiny metal surface. Carefully wipe away any loose particles from the surface of the strips.

Step E Select three clean wells in a 24-well microplate. The wells should be adjacent to each other, in a triangle.

Step F Pour 1 *M* $CuSO_4$ into one well. Pour 1 *M* $ZnSO_4$ into another well. Pour the unknown copper(II) solution into the third well.

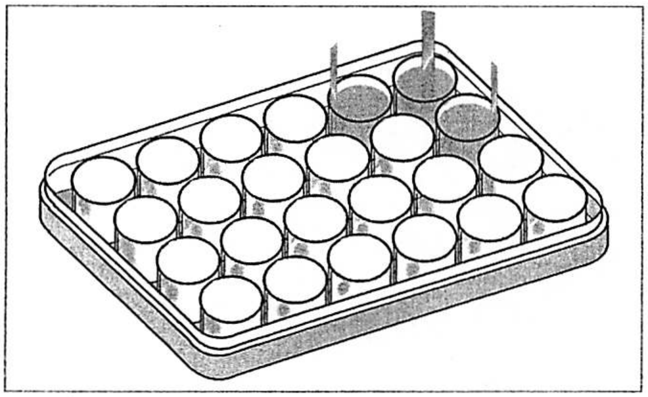

Figure 17.1

Step G Place a strip of Cu metal into each of the two wells containing Cu^{2+} solution and a strip of Zn metal into the well containing the Zn^{2+} solution. Try to stand each strip at the outer edge of its microwell, such that an equilateral triangle is formed with the metal strips at the apexes of the triangle.

II. Creating a Danielle cell

Step A With forceps retrieve one filter paper strip from the beaker of 1 *M* KCl solution. Allow excess solution to drip from the strip back into the beaker.

Step B Using the forceps, carefully drape the paper strip from the well containing 1 *M* $CuSO_4$ solution, across the top of the microwell plate, and down into the well containing 1 *M* $ZnSO_4$ solution. This paper acts as the salt bridge between the two half-cells. Do not allow the paper to contact the metal strips.

Step C Quickly attach the leads of the voltmeter to the copper strip in one well and to the zinc strip in the adjacent well.

Step D Record the voltage measured by the voltmeter.

Step E Detach the leads from the metal strips.

Step F Use forceps to retrieve the salt bridge paper strip and dispose of it properly.

III. Creating a Concentration Cell

Step A With forceps retrieve one filter paper strip from the beaker of 1 *M* KCl solution. Allow excess solution to drip from the strip back into the beaker.

Step B Using forceps, carefully drape the paper strip from the well containing 1 *M* $CuSO_4$ solution, across the top of the microwell plate, and down into the well containing unknown concentration $CuSO_4$ solution. This paper acts as the salt bridge between the two half-cells. Do not allow the paper to contact the metal strips.

Step C Quickly attach the leads of the voltmeter to the copper strip in one well and to the copper strip in the adjacent well.

Step D Record the voltage measured by the voltmeter.

Step E Detach the leads from the metal strips.

Step F Use forceps to retrieve the salt bridge paper strip and dispose of it properly.

IV. Comparing the Zn/Zn^{2+} half-cell with the unknown concentration Cu/Cu^{2+} cell

Step A With forceps retrieve one filter paper strip from the beaker of 1 *M* KCl solution. Allow excess solution to drip from the strip back into the beaker.

Step B Using forceps, carefully drape the paper strip from the well of unknown *M* $CuSO_4$ solution, across the top of the microwell plate, and down into the well containing 1 *M* $ZnSO_4$ solution. This paper acts as the salt bridge between the two half-cells. Do not allow the paper to contact the metal strips.

Step C Quickly attach the leads of the voltmeter to the copper strip in one well and to the zinc strip in the adjacent well.

Step D Record the voltage measured by the voltmeter.

Step E Detach the leads from the metal strips.

Step F Use forceps to retrieve the salt bridge paper strip and dispose of it properly.

Step G Dispose of all solutions as directed by your instructor. Rinse and dry the metals strips, since they are reuseable.

Calculations

1. Use a Table of Standard Reduction Potentials to calculate the cell potential (as voltage) of a Danielle cell.
2. Compare the cell potential that you measured with a voltmeter to that calculated with SRP values. Calculate percent error.
3. Use the voltages that you measured with the concentration cell (Procedure III) and the Danielle cell (Procedure II) to calculate the molarity of Cu^{2+} ion in the unknown.
4. Use the voltage that you measured with the cell in Procedure IV and that of the Danielle cell to calculate the molarity of Cu^{2+} ion in the unknown solution.

Post-Lab Questions

1. Write a balanced chemical equation to show the reaction that occurs in a Danielle cell.
2. Write the line notation shorthand for the Danielle cell.
3. Did the voltage that you measured with a voltmeter match the cell potential that you calculated from SRP values? Explain why the two might not have matched.
4. For each of questions 4a through 4e, explain your reasoning. Predict the effect on the cell potential of the Danielle cell if you
   a. increased the molarity of the Cu^{2+} ion

Post-Lab Questions *(continued)*

b. increased the molarity of the Zn^{2+} ion

c. poured K_2CO_3 solution into the $CuSO_4$ solution

d. increased the size of the metal strips

e. increased the temperature to 35°C

5. Did you find the same concentration for the unknown Cu^{2+} solution in Calculation 3 and Calculation 4? Would you expect to find the same value? Explain.

6. Based on your observations and calculations in this experiment, which is the more active metal, copper or zinc? Explain your reasoning.